

Application No. 09/435,748

REMARKS

Claims 29-44, 52-54 and 58-77 are pending. The specification has been updated to insert patent numbers for references to pending applications that have recently issued. Claims 38 and 54 have been amended to correct typographical errors. Claim 29 has been amended to more particularly point out the claimed invention. Applicants assert that the amendment of claim 29 inserted within the claim a feature that was inherent in the claim prior to the amendment in view of the description in the specification. The amendment of claim 29 is supported by the specification, for example, at page 7, lines 3-4 and page 8, lines 12-32. The amendments of claims 29, 38 and 54 are not intended to narrow the claims.

New claim 58 is supported by the specification, for example, at page 8, lines 12-18. New claim 59 is supported by the specification, for example, at page 2, line 28 to page 3, line 4 and page 8, lines 12-18. New claims 60-77 correspond with claims 30-44 and 52-57. No new matter is introduced by the amendments or by the new claims.

Applicants thank the Examiner and Primary Examiner Carol Chaney for the courtesy extended to Applicants' undersigned representative in a telephonic interview on October 7, 2002. Applicants' representative and the Examiners discussed in detail distinctions between Applicants' claimed invention and the disclosure in the art. Potential approaches to clarify these distinctions were discussed. Furthermore, the nature of materials generated by sputtering was discussed in order to evaluate the differences between the structures described in the Oak Ridge Bulletin and Applicants' specification. While final agreement was not reached, potentially fruitful approaches for advancing the case relating to clarifications of the claim language were discussed.

Claims 29-44 and 52-54 stand rejected. Applicants respectfully request reconsideration based on the following remarks.

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Rejection Under 35 U.S.C. § 103

The Examiner rejected claims 29-44 and 53-54 under 35 U.S.C. § 103(a) as being unpatentable over the Oak Ridge National Laboratory Bulletin, 9/1/1998 in view of U.S. Patent 5,482,797 to Yamata et.al. In this Preliminary Amendment, Applicants reply to the comments in the Advisory Action of September 6, 2002 and issues raised in the phone interview of October 7, 2002. Furthermore, Applicants have amended claim 29 for clarity. Applicants incorporate by reference arguments from the Amendment After Final of May 10, 2002. Applicants respectfully request reconsideration of the rejection based on Applicants' remarks below.

In the Advisory Action, the Examiner maintained that a sputtering process, such as described in the Oak Ridge Bulletin, produces molecules. The pertinent issue is the nature of the resulting coating produced by the sputtering process since the battery of the Oak Ridge Bulletin is formed from the coating. Applicants attach a textbook description of the sputtering process showing that the sputtering process forms a continuous layer and not a layer of particles. See Figure 6-14 (h). This continuity results from the deposition of atoms or highly reactive radicals that coalesce upon contact and dissipation of kinetic energy. Thus, the Oak Ridge Bulletin simply does not teach or suggest particles in an electrode of a battery as featured in Applicants' specification.

In the phone interview, the Examiners indicated that crystallites in a polycrystalline film formed by sputtering could be considered particles. As described in Applicants' specification, particles are described as elements of a powder. For example, see throughout and, in particular, page 7, lines 3-4, page 8, lines 12-32, page 36, lines 24-34, page 37, lines 6-19, page 45, lines 5-25 and page 52, line 33 to page 53, line 30. Thus, the claim 29 clearly corresponds to structures that are distinct from structures formed by sputtering as disclosed or suggested by the cited references.

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Furthermore, the Advisory Action asserted that "the supporting reference teaches individual particles with a diameter of less than 500 nm which one of ordinary skill in the art can combine to form a thin film electrode of less than 10 microns." However, the supporting reference (presumably the Yamada patent) does not disclose thin film electrodes with a thickness less than 10 microns. The Oak Ridge Bulletin does not disclose particles in the form of immobilized powders in an electrode layer. Therefore, the combination suggested by the Examiner can only be based on hindsight using Applicants' own specification as a template since the references do not themselves suggest the combination.

In addition, while the references do not suggest or motivate the combination indicated by the Examiner, even if they did *arguendo*, they do not provide any guidance on how to form the claimed structures. Specifically, the references do not provide a reasonable expectation of success since the references do not teach how to form thin layers comprising particles/powders, as claimed by Applicants. Therefore, the Examiner's asserted combination does not provide a reasonable expectation of success without the expenditure of inventive activity to elucidate Applicants' invention.

Thus, Applicants maintain that the Examiner has failed to establish prima facie obviousness. Applicants respectfully request withdrawal of the rejection of claims 29-44 and 53-54 under 35 U.S.C. § 103(a) as being unpatentable over the Oak Ridge National Laboratory Bulletin, 9/1/1998 in view of U.S. Patent 5,482,797 to Yamata et al.

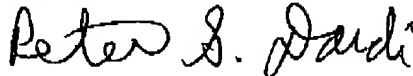
CONCLUSIONS

In view of the foregoing, it is submitted that this application is in condition for allowance. Favorable consideration and prompt allowance of the application are respectfully requested.

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The Examiner is invited to telephone the undersigned if the Examiner believes it would be useful to advance prosecution.

Respectfully submitted,



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Registration No. 39,650

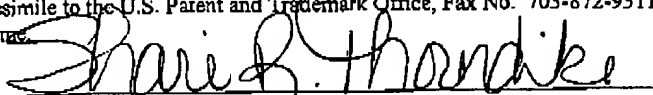
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October 28, 2002
Date


Shari R. Thorndike

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APPENDIX
MARKED-UP AMENDMENTS

IN THE SPECIFICATION

At page 35, lines 13-33, the paragraph has been amended as follows. This paragraph was previously amended in the Amendment filed on October 15, 2001.

The conditions to convert crystalline VO_2 to orthorhombic V_2O_5 and 2-D crystalline V_2O_5 , and amorphous V_2O_5 to orthorhombic V_2O_5 and 2-D crystalline V_2O_5 are described in copending and commonly assigned U.S. Patent application serial number 08/897,903, now U.S. Patent 5,989,514 to Bi et al., entitled "Processing of Vanadium Oxide Particles With Heat," incorporated herein by reference. Conditions for the removal of carbon coatings from metal oxide nanoparticles is described in U.S. Patent Application Serial No. 09/123,255, now U.S. Patent 6,387,531, entitled "Metal (Silicon) Oxide/Carbon Composite Particles," incorporated herein by reference. The incorporation of lithium from a lithium salt into metal oxide nanoparticles in a heat treatment process is described in copending and commonly assigned U.S. Patent Application Serial No. 09/311,506, now U.S. Patent 6,394,494 to Reitz et al., entitled "Metal Vanadium Oxide Particles," and in copending and commonly assigned U.S. Patent Application Serial No. 09/334,203 to Kumar et al., entitled "Reaction Method For Producing Ternary Particles," both of which are incorporated herein by reference.

At page 39, lines 19-26, the paragraph has been amended as follows. This paragraph was previously amended in the Amendment filed on October 15, 2001.

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Similarly, silver vanadium oxide nanoparticles have been produced, as described in copending and commonly assigned U.S. Patent Applications Serial Nos. 09/246,076, now U.S. Patent 6,225,007, and 09/311,506, now U.S. Patent 6,394,494, both entitled "Metal Vanadium Oxide Particles," both of which are incorporated herein by reference. For these materials surprisingly high specific capacities have been observed.

At page 44, lines 24-31, the paragraph has been amended as follows:

In addition, nanoparticles of noble metals, including silver, have been produced by laser pyrolysis. The production of silver particles with average diameters less than about 100 nm is described in copending and commonly assigned U.S. Patent Application Serial No. 09/311,506, now U.S. Patent 6,394,494 to Kumar et al., entitled "Metal Vanadium Oxide Particles," incorporated herein by reference.

Claims 29, 38 and 54 have been amended as follows:

29. (Twice Amended) A battery comprising:

a positive electrode;

a negative electrode; and

a separator between the positive electrode and the negative electrode,

wherein at least one of the electrodes has an average thickness less than about 10 microns and comprises a powder, the powder comprising electroactive particles having an average primary particle diameter less than about 500 nm.

38. (Amended) The battery of claim 29 wherein the positive electrode comprises a composition selected from the group consisting of vanadium oxide, silver vanadium oxide, manganese oxide,

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lithium manganese oxide, lithium titanium oxide, lithium cobalt oxide, lithium nickel oxide, iron sulfides, molybdenum sulfide and mixtures, composites and derivatives thereof.

54. (Amended) The battery of claim 29 wherein at least one electrode has effectively no electroactive particles with a diameter greater than about four times the average diameter of the collection of electroactive particles.

New claims 58-77 have been added as follows.

--58. (New) The battery of claim 29 wherein the at least one electrode further comprises a binder.

59. (New) A battery comprising:

a positive electrode;

a negative electrode; and

a separator between the positive electrode and the negative electrode,

wherein at least one of the electrodes has an average thickness less than about 10 microns and comprises a binder and electroactive particles having an average primary particle diameter less than about 500 nm.

60. (New) The battery of claim 59 wherein the positive electrode has an average thickness less than 10 microns and comprises electroactive particles having an average primary particle diameter less than about 500 nm.

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61. (New) The battery of claim 59 wherein the negative electrode has an average thickness less than 10 microns and comprises electroactive particles having an average primary particle diameter less than about 500 nm.
62. (New) The battery of claim 59 wherein both the negative electrode and the positive electrode have an average thickness less than 10 microns and comprises electroactive particles having an average primary particle diameter less than about 500 nm.
63. (New) The battery of claim 59 wherein the separator has a thickness less than about 10 microns.
64. (New) The battery of claim 59 wherein the negative electrode comprises a lithium intercalation compound.
65. (New) The battery of claim 59 wherein the negative electrode comprises lithium metal or a lithium alloy.
66. (New) The battery of claim 59 wherein the negative electrode comprises tin oxide or derivatives thereof.
67. (New) The battery of claim 59 wherein at least one of the electrodes comprises electroactive particles having an average diameter less than about 100 nm.
68. (New) The battery of claim 59 wherein the positive electrode comprises a composition selected from the group consisting of vanadium oxide, silver vanadium oxide,

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manganese oxide, lithium manganese oxide, lithium titanium oxide, lithium cobalt oxide, lithium nickel oxide, iron sulfides, molybdenum sulfide and mixtures, composites and derivatives thereof.

69. (New) The battery of claim 59 wherein the separator comprises a polymer.

70. (New) The battery of claim 59 wherein the separator comprises a nonliquid electrolyte comprising a lithium compound between the positive electrode and the negative electrode.

71. (New) The battery of claim 59 further comprising a current collector in electrical contact with the positive electrode, the current collector comprising aluminum metal, copper metal or stainless steel metal.

72. (New) The battery of claim 71 wherein the current collector is a foil or an expanded mesh.

73. (New) The battery of claim 59 further comprising a current collector in electrical contact with the negative electrode, the current collector comprising aluminum metal, copper metal or stainless steel metal.

74. (New) The battery of claim 59 further comprising a current collector comprising graphite paper, the current collector being in electrical contact with the positive electrode or the negative electrode.

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75. (New) The battery of claim 59 wherein the surface of at least one of the electrodes at the separator has a root mean square surface roughness less than about 5 microns.

76. (New) The battery of claim 59 wherein the electrodes comprise supplementary electrically conductive particles.

77. (New) The battery of claim 59 wherein at least one electrode has effectively no electroactive particles with a diameter greater than about four times the average diameter of the collection of electroactive particles.--

Glow Discharge Processes

SPUTTERING AND PLASMA ETCHING

Brian Chapman

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Preface

This book is based on a series of seminars held in 1978 and 1979. The seminars were intended to give some more insight into several practical glow discharge processes that are being increasingly used, particularly in the semiconductor industry. I hope that the text will serve as a useful general introduction to some of the scientific principles involved in these processes.

Glow discharges, like so many topics in science, are incompletely understood. Results are often misinterpreted, contradictory, or irrelevant. Glow discharge science has its own sub-language of special terms, with names that are often misleading, and with meanings which cannot be assumed to be constant from author to author! One can easily understand the need for the precision of scientific writing and sympathize with the conditions, provisos and double negatives of the author who is taking care not to make any definite statement which might be wrong. This is probably as scientific literature must be when one is close to the borders of knowledge and ignorance, but it is rather daunting to a newcomer to that particular branch of science.

Many of you will have had the experience of wanting to learn something about a particular area of science you're not familiar with, and so you go along for advice to the chap in your company or university who is considered the local expert. More often than not you come away with a list of references, in just about all of which it is assumed that you know the subject pretty well! And this is a particular problem in multi-disciplinary subjects such as sputtering where you are as likely to meet some electrical engineering phase angles as you are some organic chemistry.

This book is trying to be an introductory book. It attempts to thread a path through all the basic material you need before you can read the much more erudite reviews on the subject. In an effort to spare readers from attacks of mental indigestion, I have selected those aspects which appear to be more useful for first-time acquaintance, and even these are dealt with too briefly.

This text was written for readers with a wide range of backgrounds, and the emphasis is on concepts rather than on rigorous detail. I have usually restricted discussions to the general application of an idea, and have often ignored excep-

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Chapter 6. Sputtering

"WHAT IS ALL THIS SPUTTERING NONSENSE ANYWAY?"

A few years ago, a medical conference and a sputtering conference were taking place simultaneously at Imperial College. The conferees were as always demonstrating the well-known scientific phenomenon that conference systems tend towards a condition of being in the bar, where a well-oiled medic accosted a group of the sputterers and demanded to know "What is all this sputtering nonsense, anyway?" "Well", replied one of the sputterers, "we're in a branch of the medical profession too, old chap - in speech therapy actually. Sputtering's like stuttering, you know, except our chaps say p . . . p . . . p . . . p . . . instead of t . . . t . . . t . . . t . . .". The medic warmly thanked his newly-discovered professional colleague and hurried back to enthusiastically convey the freshly-gleaned information to his cronies.

The medic might have been a bit closer, though not very much, if he had looked in the dictionary. It seems that the word 'sputter' appeared in the English language (The Shorter OED, 1959) as early as 1598 and is adapted from the imitative words 'sputteren' in Dutch and 'sputteren' in West Frisian. 'To spit out in small particles and with a characteristic explosive sound', says the dictionary; 'to utter hastily and with the emission of small particles of saliva, to ejaculate in confused, indistinct or uncontrolled manner, especially from anger or excitement - His tongue was too large for his mouth; he stuttered and sputtered (1878)'.

Compared with the above, you may be disappointed with the type of sputtering I'm going to describe. I must confess that I have never heard the sound of sputtering, although the sound of rotary pumps will ring in my ears forever. On the other hand, my type of sputtering is rather colourful!

INTERACTIONS OF IONS WITH SURFACES

Let us consider what happens when an ion approaches the surface of a solid (of the same or different material); the solid is usually called the *target*. One or all of the following phenomena may occur (Figure 6-1):

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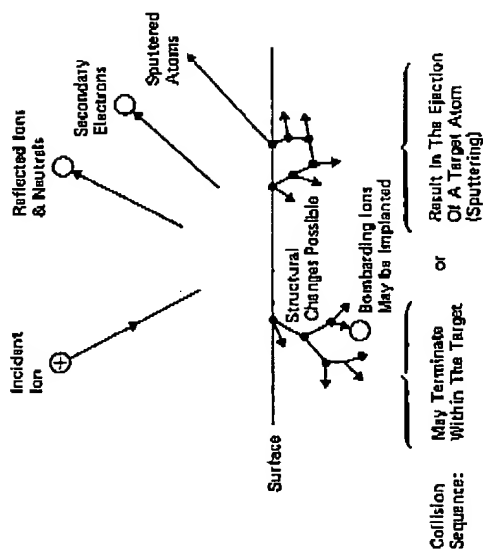


Figure 6-1. Interactions of ions with surfaces

- The ion may be reflected, probably being neutralized in the process. This reflection is the basis of an analytical technique known as *Ion Scattering Spectroscopy*, which enables us to characterize the surface layers of the material, and also tells us a lot about the fundamental ion-surface interaction.
- The impact of the ion may cause the target to eject an electron, usually referred to as a *secondary electron* (Chapter 4, "Secondary Electron Emission").
- The ion may become buried in the target. This is the phenomenon of *ion implantation*, which is already used extensively in integrated circuit technology for selectively doping silicon wafers with precisely controlled amounts and depth profiles of specific impurities, and is likely to find many other applications such as surface treatment of steels.
- The ion impact may also be responsible for some structural rearrangements in the target material. 'Rearrangements' may vary from simple vacancies (missing atoms) and interstitials (atoms out of position) to more gross lattice defects such as changes of stoichiometry (i.e. relative proportions) in alloy or compound targets, or to changes in electrical charge levels and

INTERACTIONS OF IONS WITH SURFACES

distributions, and are usually collectively referred to as *radiation damage*, which is a subject of great importance, particularly with relation to nuclear energy. Radiation damage can often be removed by annealing (heat treatment) but it is not always unwanted, and perhaps the alternative name of *altered surface layers*, used mostly to describe the stoichiometry changes, is more apt.

- The ion impact may set up a series of collisions between atoms of the target, possibly leading to the ejection of one of these atoms. This ejection process is known as *sputtering*.

The Mechanisms of Sputtering

In the energy range most relevant to sputter deposition, the interaction between the impinging ion and the target atoms, and the subsequent interactions amongst the latter, can be treated as a series of binary collisions. The sputtering process is very often compared to the break in a game of atomic billiards (Figure 6-2) in which the cue ball (the bombarding ion) strikes the neatly arranged pack (the atomic array of the target), scattering balls (target atoms) in all directions, including some back towards the player, i.e. out of the target surface. In the real process, the interatomic potential function (the variation of interatomic repulsion or attraction with separation distance) is rather different from the hard sphere billiard ball case, but nevertheless the billiard model is not too unrealistic.

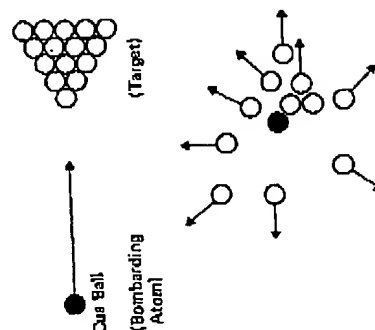


Figure 6-2. Sputtering - the atomic billiards game

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It is implied in our description of the basic interaction that the incident particle could be either an ion or a neutral atom. Ions are normally used since they can easily be accelerated by an electric field, whereas neutrals pose a problem in this respect. Furthermore, the ions are likely to be neutralized anyway by the Auger emission of an electron from the target as the ion approaches, so that the impacting species are actually mostly neutral.

The series of collisions in the target, generated by the primary collision at the surface, is known as a *collision cascade* (Figure 6-1). It will largely be a matter of luck whether this cascade leads to the sputter ejection of an atom from the surface (which will require at least two collisions) or whether the cascade heads off into the interior of the target, gradually dissipating the energy of the primary impact, ultimately to lattice vibrations, i.e. heat. It's not surprising then that sputter ejection is rather inefficient, with typically 1% of the incident energy reappearing as the energy of the sputtered atoms.

The collision phenomena occurring in a target, often referred to as *target kinetics*, are a fascinating and important subject for study. They relate not only to sputter deposition and etching, but also to ion implantation and radiation damage. Life is rather short, however, and there is neither room in this book nor am I adequately informed to pursue the topic much further. But in this chapter we shall be looking at the applications of sputtering rather than the collision phenomena leading to sputtering, and fortunately we need consider only certain aspects of the process in order to do this. In the next section we shall look briefly and (unfortunately) superficially at some of the quantitative relationships involved in sputtering target kinetics.

Sputtering Target Kinetics

A generalized treatment of target collision phenomena would have to consider the detailed interatomic potential function, but fortunately the interactions in a sputtering target are sufficiently short range that we need consider interactions only between immediate neighbours (including the incident ion). A binary collision is characterized by the energy transfer function which we met earlier (Chapter 1, "Energy Transfer in Binary Collisions"):

$$\frac{4m_i m_t}{(m_i + m_t)^2}$$

where m_i and m_t are the masses of the colliding atoms. The sputtering process is the result of a series of such collisions. A detailed consideration and experimentation show that the binary model is a useful representation of the interactions under sputtering conditions.

A useful parameter that we shall encounter frequently is the *sputtering yield* S , defined as the number of target atoms (or molecules) ejected per

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incident ion. From our model above, we would expect the sputtering yield to depend on the masses of the incident ion and the target atom, m_i and m_t respectively, and on the energy E of the incident ion. However, consider sputtering as the overall process of transferring energy from the incident ion to the sputtered atoms. Then, since the sputtered atoms can come only from the surface layers of the target, it is not just a question of transferring energy to the target atoms, but also that this energy should be transferred mostly to the surface layers. We would therefore expect the sputtering yield S to be proportional to the energy deposited in a thin layer near the surface, and this is determined by the *nuclear stopping power* $s(E)$; for low bombardment energies up to about 1 keV, an expression due to Sigmund (1969), which not surprisingly involves the energy transfer function, is

$$s(E) = \frac{m_i m_t}{(m_i + m_t)^2} E \times \text{constant}$$

and this is used to predict the following form for the sputtering yield S :

$$S = \frac{3\alpha}{4\pi^2} \frac{4m_i m_t}{(m_i + m_t)^2} \frac{E}{U_0}$$

Here U_0 is the surface binding energy of the material being sputtered, and α is a monotonic increasing function of m_i/m_t which has values of 0.17 for $m_i/m_t = 0.1$, increasing up to 1.4 for $m_i/m_t = 10$.

This expression for S predicts that the yield will increase linearly with E . In practice, this seems to be satisfied up to above 1 keV, above which S becomes relatively constant; Figure 6.3a is typical. It appears that the higher input energy is being distributed through a larger volume, so that the energy transmitted to the surface layers remains virtually constant. At very high energies, S even decreases as ion implantation becomes dominant (Figure 6-3b).

So our original expression for S is apparently valid only up to about 1 keV, and this is due to various assumptions about the atomic interactions. Above 1 keV, a modified interaction yields

$$S = 3.56\alpha \frac{Z_1 Z_2}{(Z_1^{2/3} + Z_2^{2/3})} \frac{m_i}{(m_i + m_t)} \frac{s_n(E)}{U_0}$$

where $s_n(E)$ is a reduced stopping power and is a function of a reduced energy based on the actual energy, masses and atomic numbers Z_1 and Z_2 of the atoms involved. The interested reader is referred to Winters (1976) for further details.

The success of these theoretical models can be demonstrated by comparing experimental and theoretical results, with good agreement resulting in most cases. This is illustrated in Figure 6-4 for the case of argon on copper, which compares the yield predicted by the equation above, with experimental values.

SPUTTERING

bly present, e.g. due to electrical isolation between the substrate and a thermocouple pressed down onto it, or due to thermal isolation between a substrate and the substrate platform. In this latter case, the problem arises because the substrate will generally make only three point contact to the substrate holder; it is sometimes possible to fill the intervening space with a suitable heat-conducting liquid or solid such as gallium, in order to heat-sink the substrate to the holder, but this is usually inconvenient and would be unacceptable in manufacturing processes.

The problem is exacerbated by the power input to the substrate from the glow discharge, which is liable to make the surface temperature greater than that of its bulk. The use of a thin film thermocouple evaporated onto the surface of the substrate has been proposed as a solution to this difficulty, but this is not very convenient. An alternative is to use an infra red thermometer that measures the infra red radiation emitted by the substrate; one needs to know the transmission characteristics of the window through which observation is made, but often this can be done empirically.

So it seems that measurement of the absolute substrate surface temperature is quite a difficult matter, although practically it is possible to reproduce the same conditions from run to run.

Electrode Voltage Measurement

Although many rf systems are controlled by the power input to the matching network and process chamber, some people prefer to measure and control with the target voltage since this eliminates the uncertain power losses in the matching network. It is more usual to measure the dc offset voltage, although the rf peak-to-peak is sometimes used. The dc voltage is normally obtained by filtering out the rf components with an LC circuit, as in Figure 6-12. The rf voltage waveform can be observed by using a high voltage probe (which is essentially a resistive network voltage divider) to reduce the rf signal to a suitable size for display on an oscilloscope. The probe is essentially a resistive or capacitive network voltage divider; if the ac and dc components of the waveform are required, the resistive type should be used. If only the rf peak-to-peak magnitude is required, a clamping circuit can be used, preferably immediately after the probe to avoid long leads carrying rf.

John Vossen has pointed out that when insulating targets are used, the dc offset voltage depends on leakage around the target edge to the backing plate; the unreliability of this can be avoided by using the peak-to-peak voltage. It is not clear to me why this leakage does not change the sputtering rate, if it really does change the target surface potential.

Whatever parameter is measured, care is required, both in safety and in interpretation. There are large rf currents flowing in the external circuitry, and the

SPUTTERING AS A DEPOSITION PROCESS

inductance of even a straight piece of wire can become significant at radio frequencies. These combine to cause significant drops along current-carrying connecting cables, particularly that between the matching network and the target. One can observe these voltage changes with the probe... carefully. To obviate this problem, the probe should be attached to the back of the electrode.

All of the same considerations apply to the measurement of substrate voltage, which is almost always done in a bias sputtering system by measuring the dc offset of the applied rf.

At both electrodes, the sheath voltage is determined by the difference between plasma potential and electrode potential, as discussed in previous chapters. Christensen and Brunot (1973) have proposed a method of monitoring the sheath voltage continuously (their technique is discussed in Chapter 5) but this method has not been generally adopted. Target voltage is instead used to reproduce conditions rather than give absolute magnitudes.

SPUTTERING AS A DEPOSITION PROCESS

The current main application of sputtering is for the deposition of thin films.

Thin Film Formation

In sputter deposition, as with the other standard vacuum deposition process of evaporation, material arrives at the substrate mostly in an atomic or molecular form (Figure 6-14). The atom diffuses around the substrate with a motion determined by its binding energy to the substrate and is influenced by the nature as well as the temperature of the substrate. Energetically, the surface of the substrate is like an egg carton, with each of the depressions constituting a temporary resting point or *adsorption site* for the depositing and diffusing atoms. At each 'hop', the atom will either jump over the barrier into an adjacent site, or might even hop right out of the egg carton — i.e. re-evaporate. After a certain time, the atom will either evaporate from the surface or will join with another diffusing single atom to form a doublet, which is less mobile but more stable than the single atom. I like to think of two men (please insert your favourite ethnic group) tied together inside a giant egg carton, and trying to jump over the barriers into the adjacent depressions. The chance of them being well enough co-ordinated to jump together is extremely slim, so their mobility is severely limited, as is the chance of their 're-evaporation'.

The chance of forming the atomic pair will depend on the single atom density and hence on the arrival or deposition rate. In time, the doublets will be joined by other single atoms to form triplets, quadruplets and so on. This is the *nucleation* stage of thin film growth, leading to the formation of quasi-stable islands,

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each containing tens or hundreds of atoms and typically having densities of $10^{10}/\text{cm}^2$. During the next, *island growth* stage, the islands grow in size rather than in number. Eventually they grow large enough to touch; this is the *agglomeration* or *coalescence* stage. From observations in the transmission electron microscope, it appears that the islands often display liquid-like behaviour during coalescence, and there are often crystallographic reorientations as a result of competition between the structures of the coalescing islands. Coalescence proceeds until the film reaches *continuity*, but this may not occur in some cases until the film is several hundred Ångströms in average thickness. During the coalescence stages, the film therefore typically consists of hills and valleys.

During the island stage, each island is usually single crystal or contains just a few crystals. On a polycrystalline substrate, the orientation of each island will be random, so that the resulting film is polycrystalline. On a single crystal substrate, the island orientations may be determined by the substrate structure so that growth and coalescence leads to a single crystal film. This is the phenomenon of *epitaxy* (Bauer and Poppa 1972).

If surface atoms are mobile, they have a greater opportunity of finding low energy positions, consistent with crystal growth, in the growing film. Mobility is enhanced by increased substrate temperature. But since it also takes time to find an energetically favourable lattice position, crystal growth is also encouraged by low deposition rates. Hence, on single crystal substrates, for each deposition rate there will be a temperature, the *epitaxial temperature*, above which single crystal films can be grown.

It is more likely that polycrystalline films on polycrystalline substrates will be required. During the island stage, each island will contain one or a few crystallites. The same mechanisms obtain as in single crystal growth, so that high substrate temperature and low deposition rate lead to large grains, low density of crystal defects, and large film thickness for continuity. The reverse (low temperature and high rate) associations are also generally true.

All of the relationships above were found for the comparatively simple case of deposition by vacuum evaporation. The structure of the growing film was found to be extremely sensitive to deposition conditions. Electron bombardment either prior to or during deposition was found to encourage film continuity and reduce epitaxial temperatures (Stirland 1966). Ion bombardment (Wehner 1962) and increased arrival energy of the depositing atoms (Chapman and Campbell 1969) also reduced the epitaxial temperature.

Life on the Substrate

The purpose of the preceding discussion was to illustrate the very sensitive dependence of thin film structure on growth conditions, even for deposition by

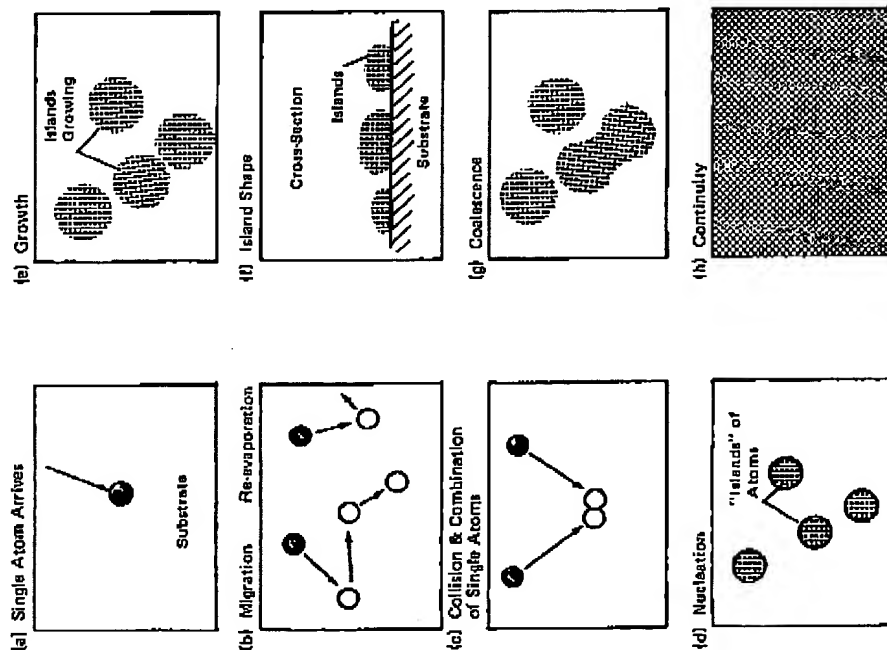


Figure 6-14. Formation of a thin film (Leaver and Chapman 1970)

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evaporation. By contrast, the sputtering environment is extremely complex and has many variables.

Figure 6-15 shows a substrate on which we wish to deposit a sputtered film. We have seen that the nature and temperature of the substrate are important in determining the nature of the film. During thin film growth, the substrate and growing film will be subjected to many types of bombardment (Figure 6-16) which will now be described.

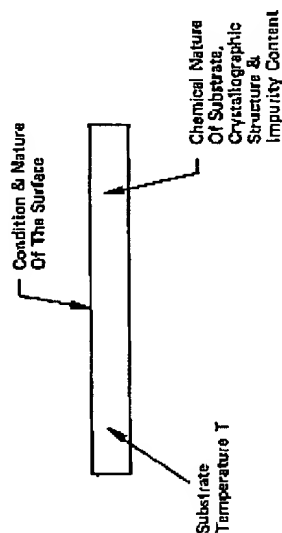


Figure 6-15. The influence of the substrate on thin film structure

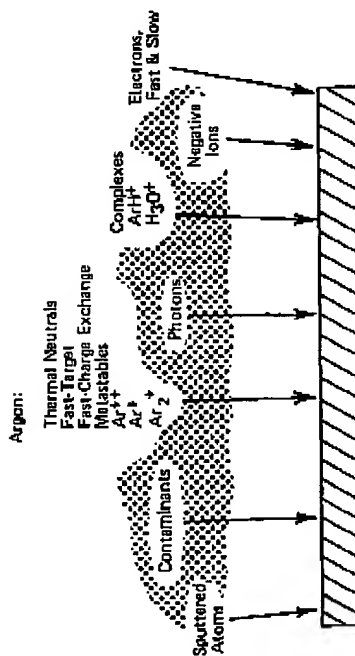


Figure 6-16. Particles bombarding the substrate in sputter deposition

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Sputtered Atoms and Contaminants

Let's refer again to the example given in Chapter 1, "Monolayer Formation Time". A typical sputter deposition rate is one monolayer per second, i.e. $\sim 10^{15}$ atoms/cm² second or 200 Å/minute for a 'typical' atom of about 3 Å diameter. A contaminant gas having a partial pressure of 10^{-6} torr will contribute a numerically equal flux at the substrate. Such contamination will be particularly effective if it is chemically active. The example in Figure 6-17 is from deposition by evaporation, at a higher rate (1200 Å/min) than the sputtering example, but the point is the same; the aluminum film begins to oxidize at an oxygen pressure $\sim 10^{-7}$ torr. We must remember that a contaminant partial pressure of 10^{-6} torr in a total sputtering pressure of 20 mtorr amounts to a contamination level of only 50 ppm! We are unlikely to achieve such a low level, and the contaminant flux will increase proportionately with its partial pressure. If the contamination results from an internal source such as outgassing from a heated substrate, then its partial pressure (which results from an equilibrium between the rates of introduction and pumping) can be minimized by maximizing the pumping rate and hence gas flow rate. (See Chapter 1, "Conductance"). But this expedient is ineffective if the contamination is introduced with the gas, indicating a vital need for pure sputtering gas.

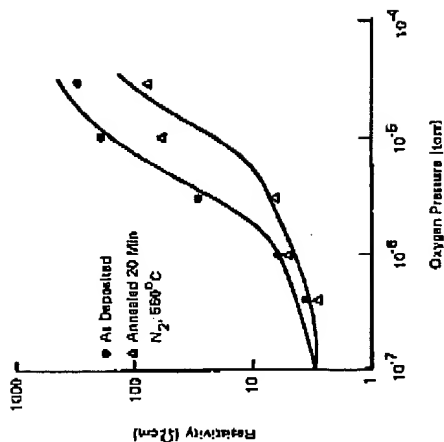


Figure 6-17. Room temperature reactivity vs oxygen pressure during evaporation of 5000 Å aluminum films at 200° C and 20 Å/sec (d'Heurle et al. 1968)

Sputtering Gas Atoms — Fast and Slow

Compared with the fluxes of sputtered atoms and contaminants at the substrate, the flux of argon (or other sputtering gas) is truly enormous. At 20 millitorr, the argon flux would be about 10^4 times greater than the arrival rate of sputtered material. It would not be surprising, therefore, if argon were trapped in the growing film. Indeed, trapped argon is observed in sputtered films (Winter and Kay 1967), although not for the obvious reason. Winters and Kay evaporated a nickel film under similar conditions of argon pressure and deposition rate as for the sputtered films, but found that the argon content in the evaporated films was very much lower ($< 1\%$).

They determined the content of their nickel films by vaporizing the film and measuring the resultant gas evolution with a mass spectrometer. The argon content was measured as a function of substrate temperature (Figure 6-18) and total argon pressure (Figure 6-19). The temperature dependence is as expected; argon is likely only to be physisorbed, so is less likely to be initially adsorbed and more likely to be subsequently desorbed, with increasing substrate temperature.

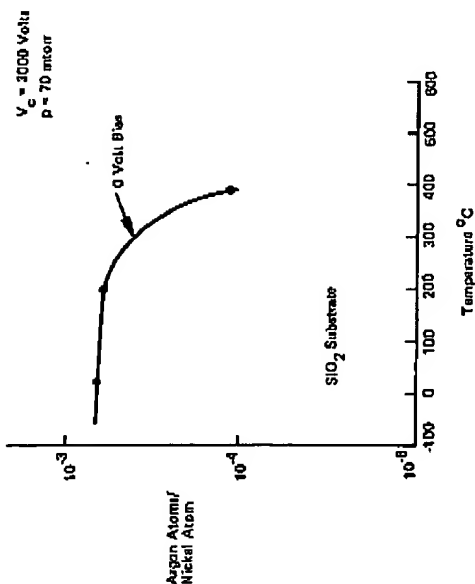


Figure 6-18. Argon content in sputtered nickel films as a function of deposition temperature (Winters and Kay 1967)

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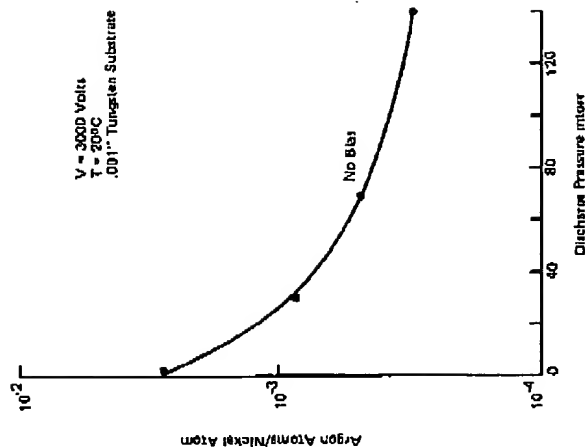


Figure 6-19. Argon content in sputtered nickel films as a function of argon discharge pressure (Winters and Kay 1967)

The pressure dependence (Figure 6-19) is rather interesting. The effect is ascribed to the small flux of high energy argon neutrals striking the substrate, rather than the large flux of thermal neutrals. Energetic argon ions striking the target are neutralized in the process and rebound as energetic neutrals. These energetic neutrals, arriving at the substrate, are likely to be embedded in the growing film; Comas and Wolke (1970) have demonstrated how argon ions are entrapped in silicon, and fast neutrals are likely to behave in a similar way. Travelling across the sputtering chamber, the energy of these fast neutrals is attenuated by gas phase collisions and so their incorporation into the growing film (per unit film atom) decreases with increasing pressure.

One would expect fast neutrals to have a smaller collision cross-section than thermal neutrals. The existence of fast electrons and negative ions from the target similarly traversing the sputtering system without collision and bombarding

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the substrate has been clearly demonstrated, as is discussed later. In the Winters and Kay work there is apparently an effect of the fast neutrals even at a pressure of 100 mtorr. Since there will be about one fast neutral leaving the target for each sputtered target atom, the measured argon content of $\sim 10^{-4}$ argon atoms per nickel atom at 100 mtorr (Figure 6-19) implies that at least this proportion reach the substrate with enough energy left to be adsorbed. Based on collision probabilities (Chapter 1), this is a little surprising, but one can't argue with the results. It is presumably a manifestation of the lower collision cross-section and pronounced forward scattering that one expects for higher energy particles (see Appendix 4).

Excited Neutrals

To return to Figure 6-16, we have so far been considering bombardment by ground state neutrals. A further source of bombardment is due to excited neutrals, of which metastables of the sputtering gas would be most abundant. These can presumably lose their potential energy at the growing film and hence influence its growth, although Kaminsky (1965) indicates that these metastables should be resonance ionized and Auger neutralized before they reach the substrate.

Positive Ions

In addition to these neutrals, there will be bombardment by charged particles. Argon ions will be the most abundant positive ions, with a flux of the order of $n\bar{c}/4$. The figure of $20 \mu\text{A}/\text{cm}^2$ from our example in Chapter 3 corresponds to a flux equivalent to a few tenths of a monolayer per second. There will also be ions of the sputtered material, produced both by electron impact ionization and by the Penning process of collision with metastables (Chapter 2, "Metastable Collisions"). These ions, and any others, will be accelerated across the sheath at the substrate. Under normal conditions, the sheath will be quite thin and there will be little attenuation of the ions due to collisions in the sheath.

Valuable information about ion bombardment at the substrate has been acquired via the work of John Coburn (1970 et seq.), who has been able to analyze the energy and mass of ions striking the substrate. His work is described in more detail in the section on bias sputtering. For now, we note that he was able to identify contaminant ions, the less abundant argon ion species such as Ar^{2+} and Ar^{3+} , and also complex ions such as ArH^+ and short-lived ions such as H_3O^+ . (We discussed in Chapter 2 how ions can change their chemical identity as their electronic shell structure changes). So we have to add these ions to our list in Figure 6-16.

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Negative Ions

Negative ions of the target material may form also. The space charge sheath established at the substrate will tend to repel and slow down these ions, but they will still reach the substrate if they are energetic enough (which will be so if they're formed at the target or in the target sheath). Negative ions at the substrate were detected by Koenig and Maisel (1970) in their work on sputtered quartz. Harek and Pellicane (1976) have shown how fast negative ions from the target can sputter etch the substrate, and their findings have been confirmed more recently by the experimental work of Cuomo et al. (1978) and the theoretical work of Robinson (1979). Presumably, negative ions can also be formed from gas phase contaminants, although they would be energetic enough to reach the substrate only if they were formed in the target sheath.

Electrons

A major source of charged particle bombardment at the substrate is due to electrons. With a conducting substrate, the average current density will be about $1 \text{ mA}/\text{cm}^2$, which is equivalent to $6.25 \cdot 10^{15}$ electrons/ cm^2 second or a few electrons for each depositing atom. The majority of these electrons will be thermal electrons from the glow where they have energies of a few electron volts (Chapter 3), although only the more energetic of them will be able to surmount the sheath at the substrate. An insulating substrate on the anode in a dc discharge will charge up to floating potential and will receive a much smaller electron flux, equal to the ion flux.

In addition to these slow electrons, there will be bombardment by fast electrons. These electrons are emitted from the target by ion and other impact, are accelerated across the target sheath, and then travel across the sputtering system without making collisions, as described in Chapter 4. So they have energies equivalent to the sheath voltage. These electrons have been detected by Koenig and Maisel (1970); their results in an rf system, obtained by retarding potential measurements, are shown in Figure 6-20. Ball (1972), again using a retarding potential technique but in a dc system, obtained the results shown in Figure 6-21; these results suggest that a large fraction of the electrons striking the substrate have almost the full target sheath voltage, but it is not clear that an allowance was made for the transmission of the analyzer.

The energy spectrum of electrons bombarding the anode has also been measured by Leopoldo Guimaraes (Chapman et al. 1974) using the apparatus shown in Figure 6-22. Typical results for the collector current as a fraction of the total current, using a copper target, are shown in Figure 6-23. For reasons involving the resolution and mode of use of the analyzer, these curves do not show electron flux against energy but rather power input to the substrate due to charged

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electron bombardment pattern as the sputtering conditions were varied. The threshold for glowing was at several hundred volts, so that only fast electrons were detected by the screen. The screen glowed very brightly opposite the glass sections of the copper/glass target. Figure 6-25a is a photograph of the fluorescent screen taken at an angle of about 45° through the vacuum chamber wall. The pattern on the screen could easily be deflected with a weak magnetic field (Figure 6-25b), showing the particles to be electrons rather than much heavier (and hence more difficult to deflect) ions.

These fast electrons can have a major influence on the structure and properties of the growing film on the substrate. The large energy input causes a good deal of substrate heating, and there are more subtle effects due to the electron interaction with the surface, as discussed in "Thin Film Formation". These electrons have been observed to discourage as well as enhance thin film growth (Chapman et al. 1974).

Photons

The final type of bombardment that the substrate experiences is due to photons. Photons can be produced by ion or electron bombardment on any surface, and the photon can be as energetic as the ion or electron producing it, which therefore means a thousand electron volts or more in a sputtering system. Such energies put these photons in the soft x-ray class. Lower energy photons will also result from relaxation of excited atoms in the glow.

We have already discussed how photon bombardment can cause electron emission from a surface, and I would be surprised if these photons did not affect the growth of a film, as does every other type of energy input to the substrate. However, there appears to have been very little work on photon effects in thin film growth.

Radiation Damage: Creation and Removal

There is a recent paper by DiMaria et al. (1979) on neutral charge traps produced in silicon dioxide films, actually in a reactive ion etching system which is nevertheless very much like a sputtering system. By measuring the centroid of the damage, they concluded that this damage was due to soft x-rays rather than charged particle bombardments. This conclusion is consistent with the additional observation that similar damage could be produced with the substrate anywhere in the system; photons, being uncharged, bombard all surfaces within the system. DiMaria et al. also found more gross damage at the surface of their samples, which they concluded was due to energetic ion, neutral, and electron bombardment. Their results are consistent with the earlier work by Hickmott (1969), who studied radiation damage in rf sputtered SiO_2 films.

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particle bombardment versus particle energy, or, more precisely, $dP(E)/dE$ vs. E , where $dP(E)$ is the power carried to the electrode by particles with energies between E and $E + dE$. The flux distribution can be unravelled by noting that $dP(E) = E \cdot dN(E)$. The peak of the flux distribution occurs at quite low energy as expected, but there are a significant number of negative particles, which appear to be secondary electrons emitted from the target, that travel from the target to the substrate without making collisions, and hence travelling along the essentially straight field lines; we discussed these fast electrons in Chapter 4. This collision-free electron travel is presumably a manifestation of the total collision cross-section for electron scattering in argon (Figure 2-27) becoming quite small for electron energies above about 100 eV. However, although small in number, these electrons are responsible for almost all of the power input into the substrate. (The ion-electron recombination energy can also be considerable, amounting to 4.5 mW/cm^2 for an ion current component of 0.3 mA).

In the same series of experiments, a composite sputtering target of copper and glass (Figure 6-24) was used in an rf sputtering system. The glass had a much larger secondary electron coefficient than the copper. The electron emission pattern was directly observed by coating a glass substrate with a fluorescent material and placing this on the counterelectrode of the sputtering system, several inches from the target. It was then possible to directly observe changes in the

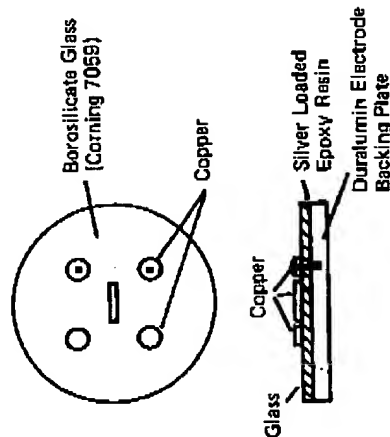


Figure 6-24. Composite sputtering target for secondary electron experiments (Chapman et al. 1974)